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Photo-Ordering and Deformation in Azobenzene-Containing Polymer Networks under Irradiation with Elliptically Polarized Light

Vladimir Toshchevikov ¹ and Marina Saphiannikova ^{2,*} 
¹ Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi pr. 31, 199004 Saint-Petersburg, Russia

² Leibniz-Institut für Polymerforschung, Hohe Str. 6, 01069 Dresden, Germany

* Correspondence: grenzer@ipfdd.de

Abstract: Azobenzene-containing polymers (azo-polymers) have been a subject of extensive investigations during the last two and half decades, due to their remarkable ability to undergo pronounced alignment and deformation under irradiation with light. The molecular ordering and deformation in azo-polymers of various structures under irradiation with linearly polarized light was described in a series of theoretical works, based on the effect of the reorientation of azobenzene moieties due to the anisotropic character of the photoisomerization processes. In the present study, we generalize the previous orientation approach to describe the photo-alignment and deformation of azo-polymer networks under irradiation with elliptically polarized light. We demonstrate that, in general, the light-induced ordering and deformation have a biaxial symmetry defined by the polarization ellipse. Azobenzene chromophores have a tendency to align along the direction of light propagation, the orientation in the other two directions being dependent of the aspect ratio of the polarization ellipse. This causes deformation of azo-polymer networks along the direction of light propagation, the sign of which (expansion/contraction) is defined by a chemical structure of network strands. Theoretical results are in agreement with experiments and have a practical importance to predict the photo-mechanical response of azo-polymers depending on their structure and on the polarization of light.

Keywords: photo-active materials; azobenzene-containing polymers; polymer networks; orientation ordering; statistical physics



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1. Introduction

The transformation of energy from one type into another is one of the important topics nowadays. In particular, transformation of light energy into other types of energy is of a special interest. In this respect, azobenzene-containing polymers (azo-polymers), which are able to change their shape [1,2] and alignment [3,4] under irradiation with light, are prospective materials for photo-controllable devices, which wirelessly convert the energy of visible and ultraviolet light into mechanical force [5,6]. Quick and contactless control of the light-induced movement opens up a fascinating potential for the use of azo-polymers as light-driven sensors, actuators [7], artificial muscles [8], etc.

Using various combinations of the interfering laser beams provides a possibility to create bizarre micro- and nano-scale patterns of alignment [9,10] and deformations [11,12] on surfaces of glassy azo-polymers. Inscription of relief gratings [13,14] and alignment patterns on surfaces of azo-polymer glasses serve as a basis to use these materials as aligning layers in display and semiconductor technology, as data storage, for photonic applications [15], in 4G optics technology [16], as novel ultrathin lenses [17], patterned substrates [18], etc.

Incorporation of azo-chromophores into liquid crystalline (LC) polymers provides a possibility for more unusual macroscopic photomechanical responses of such multi-

component photosensitive materials [19,20]. As examples, one can mention a reversible bending–unbending behavior [2,5] in monodomain LC azo-containing samples under irradiation with ultraviolet and visible light. Imprinting of complex local director distributions into LC azo-polymers leads to fancy photo-responses: helical motions [21], three-dimensional fingerprints in cholesteric LC azo-networks [22], a light-driven artificial flytrap [23], and a caterpillar-like crawling and wave-like movement [24]. Interestingly, some of these motions imitate nontrivial mechanical movements of living systems [23–25].

To forecast the photo-mechanical properties of azo-polymers, a series of theoretical works was proposed by us [26–28] to explain the mechanism of light-driven mechanical response. According to modern theoretical concepts, the light-induced ordering and deformation of azo-polymers is caused by the anisotropic character of photoisomerization processes with respect to the polarization vector of light. Under irradiation with the linearly polarized light, azobenzene chromophores are transformed from the ground (rod-like) trans-state to the excited (bent) cis-state. The probability of the trans–cis photoisomerization depends on the orientation of the chromophore with respect to the polarization vector of the light, $\mathbf{E}$. Maximal probability of the trans–cis photoisomerization corresponds to the parallel orientation of the long axis of the trans-isomer with respect to the vector $\mathbf{E}$ [29–31]. After cyclic trans–cis–trans photoisomerization processes, an anisotropic steady state emerges with preferable orientation of azo-chromophores in the plane perpendicular to the polarization vector of the light. Additionally, the appearance of bent cis-isomers under irradiation with light is able to destroy the oriented state in LC azo-polymers (so-called dilution effect) and significantly change the ordering in these multicomponent materials.

To describe the light-induced orientation anisotropy appearing in azo-polymers under irradiation with linearly polarized light, it was proposed to introduce a phenomenological orientation potential acting on each azo-chromophore [26,27]:

$$U(\theta) = V_0 \cos^2 \theta. \quad (1)$$

Here θ is the angle built by the long axis of a chromophore and the light polarization $\mathbf{E}$; V_0 is the strength of the orientation potential, which is proportional to the intensity of light, I :

$$V_0 = C \cdot I. \quad (2)$$

The use of the orientation potential in the form of Equations (1) and (2) was justified recently [28,32] by considering explicitly the kinetic equations of angular-dependent photoisomerization processes of chromophores in azo-polymers. It was shown [28] that the proportionality constant C is related to the opto-mechanical parameters of azo-polymers, such as quantum yields of the photoisomerization process, the absorption cross section of azobenzene moieties and rotational diffusion coefficient of the azo-chromophores related to the viscosity of the polymer material. Note that these material parameters can vary for various azo-polymers and it was estimated that the proportionality constant C has typical values in the range $C \cong 10^{-19}–10^{-18} \text{ J} \cdot \text{cm}^2 / \text{W}$, depending on the chemical structure of the azo-polymers [26–28].

The orientation approach based on the potential (1) allows to describe in a sufficiently simple way the main features of photo-ordering and deformation in azo-polymers avoiding costly calculations related to explicit solutions of equations of photoisomerization. This approach was successfully applied to describe the photo-mechanical properties of a broad class of azo-polymers, including uncrosslinked amorphous polymers [26,28,33], crosslinked isotropic polymer networks [27], and LC azo-containing polymer networks [32,34]. The proposed orientation approach is able to explain various experimental facts. For example, the mechanical stress provided by the orientation potential (1) is higher than the yield stress for glassy azo-polymers [26,28,35], which explains the inscription of periodical topographical structures onto glassy polymer films. Azo-polymers can display either expansion or contraction along the polarization vector $\mathbf{E}$, depending on their chemical structure in agreement with experiments [2,36]. Photo-deformation of azobenzene networks

depends on the cross-linking degree and on the amount of azobenzene chromophores [1,27]. The agreement of the theoretical approach based on the orientation potential (1) with multiple observations demonstrates its great strength to describe the photo-ordering and deformation in azo-polymers of various structures.

In the present study, we extend the orientation approach proposed earlier for linearly [26,27] and circularly [35] polarized light irradiation to describe the influence of elliptically polarized light on photo-ordering and deformation in azo-polymers. Note that the linearly and circularly polarized light irradiations represent particular cases of the light wave with elliptical polarization. Thus, the present theory provides a generalization of the orientation approach and includes the limiting cases considered earlier for linearly [26,27] and circularly [35] polarized light.

Elliptical polarization appears on surfaces of azo-polymer glasses during inscription of relief gratings and alignment patterns under irradiation with interfering beams of special combinations [37–39]. A series of experiments on photo-deformation was carried out under irradiation with unpolarized light [40,41], which can be treated as a circularly polarized light in a first approximation. Therefore, it is practically important to understand the features of ordering and deformation of azo-polymers under irradiation with light of arbitrary polarization, i.e., with elliptically polarized light in general. Note that the orientation potential (1) proposed for linearly polarized light is characterized by uniaxial anisotropy with respect to the polarization vector $\mathbf{E}$. As it is shown below, elliptically polarized light induces biaxial ordering and deformation of azo-polymers in general. The results of the present theory are important to forecast the photo-mechanical response of azo-polymers depending on their structure and polarization of light.

2. Model and Main Equations

A polymer network is modelled as an ensemble of network strands between cross-links (network junctions), see Figure 1a. A network strand is represented as a freely jointed polymer chain built from N Kuhn segments. It is assumed that each Kuhn segment contains an azobenzene chromophore in a side chain. Orientation distribution of azobenzenes around the polymer backbones is characterized by the distribution function $W(\alpha)$, where α is the angle between the long axis of the azobenzene denoted by a vector $\mathbf{k}$ and the Kuhn segment (Figure 1a). The function $W(\alpha)$ is determined by the chemical structure and the length of spacers between the backbones of polymer chains and the chromophores. Below it will be shown that photo-deformation of an azobenzene-containing polymer network is prescribed by structural parameters, related to the second moments of the distribution function $W(\alpha)$.

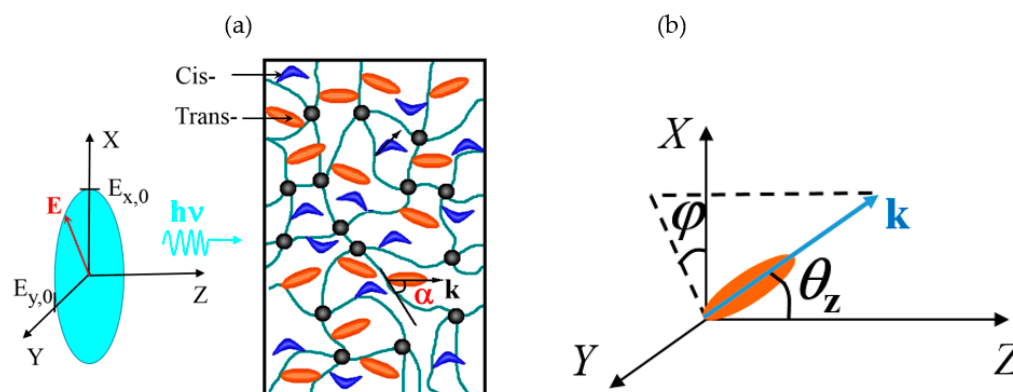


Figure 1. Model of an azobenzene-containing polymer network under irradiation with elliptically polarized light (a). Orientation of an azobenzene in the frame of references related to the elliptically polarized light (b). α is the angle built by the long axis of the chromophore denoted by a vector $\mathbf{k}$ and the Kuhn segment.

Application of the elliptically polarized light to the azo-network induces a cyclic trans–cis photo-isomerization of chromophores. This process is accompanied by alignment of the chromophores with respect to the frame of references related to the elliptically polarized light. To describe the orientation ordering of chromophores in the steady state under irradiation with elliptically polarized light, an orientation potential can be introduced similarly to linearly polarized light.

The characteristic feature of elliptical polarization is that a tip of the electric field vector of light describes an ellipse in the plane normal to the direction of the light propagation. Let us assume that the principal axes of the ellipse described by the tip of the electric field vector are directed along the x - and y -axes and the light propagates along the z -axis (Figure 1a). The elliptically polarized light can be represented as a superposition of linearly polarized waves, both propagating along the same z -axis but having the orthogonal electric vectors:

$$\mathbf{E}_x(t) = E_{x,0} \cos \omega t \text{ and } \mathbf{E}_y(t) = E_{y,0} \sin \omega t. \quad (3)$$

Here $E_{x,0}$ and $E_{y,0}$ are the magnitudes of the electric field vectors for the two linearly polarized waves; ω is the angular frequency of the light. The vectors $\mathbf{E}_{x,0}$ and $\mathbf{E}_{y,0}$ define the main semi-axes of the polarization ellipse (Figure 1a). The intensities of the two linearly polarized light waves, I_x and I_y , can be related to the total intensity of the elliptically polarized light, I :

$$I = \frac{c}{4\pi} \langle \mathbf{E}^2 \rangle = \frac{c}{4\pi} \langle \mathbf{E}_x^2 + \mathbf{E}_y^2 \rangle = I_x + I_y, \quad (4)$$

where c is the speed of light in a vacuum.

Representation of the elliptically polarized light as a superposition of two linearly polarized light waves allows to introduce an orientation potential, which reorients azobenzene chromophores in the steady state under irradiation with elliptically polarized light. The influence of both linearly polarized light waves can be described by the orientation potential according to Equations (1) and (2), so that the orientation potential of a chromophore under action of the elliptically polarized light, U_{elp} , can be written as a superposition of two contributions:

$$U_{\text{elp}}(\theta_x, \theta_y) = CI_x \cos^2 \theta_x + CI_y \cos^2 \theta_y, \quad (5)$$

where θ_β ($\beta = x, y, z$) are the angles between the long axis of a chromophore and the β -axes. For further calculations, it is convenient to introduce the two Euler angles, $\Omega = (\theta_z, \varphi)$, as presented in Figure 1b, which define the angles θ_β as follows:

$$\cos \theta_x = \sin \theta_z \cos \varphi \text{ and } \cos \theta_y = \sin \theta_z \sin \varphi. \quad (6)$$

Alternatively, the potential (5) can be rewritten as a function of the total light intensity I :

$$U_{\text{elp}}(\Omega) = CI \left[w_x \cos^2 \theta_x + w_y \cos^2 \theta_y \right], \quad (7)$$

where the dimensionless parameters $w_x = I_x/I$ and $w_y = I_y/I$ are the relative contributions of the linearly polarized waves to the total light intensity of the elliptically polarized light ($w_x + w_y = 1$). They are related to the aspect ratio of the polarization ellipse, see Figure 1a. The orientation potential in the form of Equation (7) for the elliptically polarized light reproduces two limiting cases: for the linear polarization ($w_x = 1$ and $w_y = 0$) it is reduced to the relationship (1) introduced above; for the circular polarization ($w_x = w_y = 1/2$) it reproduces the results of previous work [35]:

$$U_{\text{circ}}(\Omega) = \frac{1}{2} CI \sin^2 \theta_z. \quad (8)$$

Note that the circularly polarized beam reorients chromophores along the direction of light propagation [35].

Now, the introduced orientation potential U_{elp} allows us to derive the orientation distribution function of azobenzenes under the influence of the elliptically polarized light in the steady state:

$$f(\Omega) = Z^{-1} \exp[-U_{\text{elp}}(\Omega)/kT], \quad (9)$$

where the normalization constant Z has a form:

$$Z = \int d\Omega \exp[-U_{\text{elp}}(\Omega)/kT]. \quad (10)$$

Here the integration runs over the Euler angles: $d\Omega = \sin\theta_z d\theta_z d\varphi$, where $\theta_z \in [0, \pi]$ and $\varphi \in [0, 2\pi]$.

Using the distribution function (9), the components of the order parameter tensor [42] can be calculated: $\hat{S}_{\beta\gamma} = (3\langle k_\beta k_\gamma \rangle - \delta_{\beta\gamma})/2$. Here $k_{\beta,\gamma}$ are the components of the vector $\mathbf{k}$ (Figure 1b) and $\delta_{\beta\gamma}$ is the Kronecker delta. Since the distribution function (9) is invariant with respect to the transformation $k_\beta \rightarrow -k_\beta$, which follows from Equation (7), all non-diagonal components of $\hat{S}_{\beta\gamma}$ vanish and the order parameter tensor takes a diagonal form:

$$\hat{S}_{\beta\gamma} = \begin{pmatrix} S_{xx} & 0 & 0 \\ 0 & S_{yy} & 0 \\ 0 & 0 & S_{zz} \end{pmatrix}. \quad (11)$$

Thus, the principal axes of the order parameter tensor coincide with the principal axes related to the polarization ellipse of elliptically polarized light. A characteristic feature of the order parameter tensor is that its trace, i.e., the sum of diagonal elements, is always equal to zero. Below we discuss the results of the numerical analysis of the light-induced ordering and deformation of azo-networks and show that they have biaxial symmetry under irradiation with the elliptically polarized light.

3. Light-Induced Orientation Order

For definiteness, we will assume in the present and following sections that the polarization ellipse is prolate along the x -axis, i.e., $I_y \leq I_x$ (in other words, $w_y \leq w_x$ and $0 \leq w_y \leq 1/2$). As it was mentioned above, the limiting cases $w_y = 0$ and $w_y = 1/2$ correspond to linearly and circularly polarized light irradiation, respectively. Note that the results of the present section are rather general and illustrate the ordering behavior of azobenzene chromophores not only in cross-linked azo-networks but also in other azo-polymer systems consisting of long polymer chains (linear polymers in glassy state, in polymer melts and solutions, etc.).

Figure 2a,b shows the components of the order parameter tensor $S_{\beta\beta}$ as functions of the dimensionless parameter V_0/kT , which is proportional to the intensity of the light I , according to Equation (2): $V_0 = CI$. As example, at typical value $C = 10^{-18} \text{ J}\cdot\text{cm}^2/\text{W}$, the scale of the parameter $V_0/kT = 1$ corresponds to the light intensity $I = 4 \text{ mW}/\text{cm}^2$. The values of w_y are chosen close to the limiting cases for linearly polarized light ($w_y = 0.1$ and 0.25 , Figure 2a) and for circularly polarized light ($w_y = 0.35$ and 0.45 , Figure 2b). In Figure 2a,b, as well as in all figures below, the lines illustrate the results of theoretical calculations and the different symbols are used only to denote the results for different quantities and at different parameters. One can see in Figure 2a,b that at the absence of light, $I = 0$, the system of azo-chromophores is isotropic ($S_{xx} = S_{yy} = S_{zz} = 0$) and it becomes biaxial anisotropic ($S_{xx} \neq S_{yy} \neq S_{zz}$), when the light is switched on, $I > 0$. Biaxial ordering of azo-polymers under irradiation with light was observed in a series of experiments [29,43–45].

In both cases, presented in Figure 2a,b, the azobenzenes are aligned along the direction of light propagation ($S_{zz} > 0$) and demonstrate the ordering aside the x -axis ($S_{xx} < 0$) at $I > 0$. This result is general and can be understood from the following considerations. The orientation potential (5) can be rewritten in the following form:

$$U_{\text{elp}}(\theta_x, \theta_z) = C(I_x - I_y) \cos^2 \theta_x + CI_y \sin^2 \theta_z. \quad (12)$$

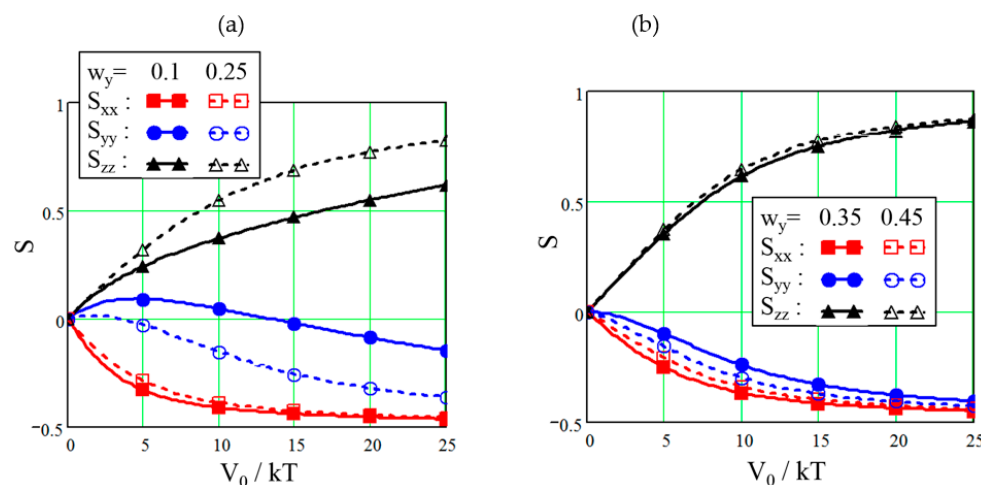


Figure 2. Components of the order parameter tensor $S_{\beta\beta}$ as functions of the parameter V_0/kT at $w_y = 0.1; 0.25$ (a) and at $w_y = 0.35; 0.45$ (b).

Here the first contribution corresponds to the influence of the linearly polarized light with the polarization vector along the x -axis ($I_x - I_y > 0$) and the second term is equivalent to the influence of circularly polarized light of intensity I_y , which propagates along the z -axis. Both these contributions reorient the azo-chromophores along the direction of light propagation (z -axis) and aside the axis with maximal polarization of elliptically polarized light (i.e., aside the x -axis). The magnitudes of S_{xx} and S_{zz} increase with increasing light intensity.

On the other hand, the two terms in Equation (12) contribute in opposite directions to the ordering of chromophores with respect to the y -axis: the first contribution reorients the chromophores along the y -axis, whereas the second one leads to the orientation of chromophores along the direction of light propagation, i.e., aside the y -axis. Thus, the ordering with respect to the y -axis is determined by the interplay between the linearly and circularly polarized beams and the value S_{yy} can be of different signs. At w_y close to $1/2$ the contribution from the circularly polarized beam provides the main effect: S_{yy} is negative and decreases with increasing light intensity (Figure 2b). At small w_y the value S_{yy} demonstrates nonmonotonic dependence as a function of light intensity (Figure 2a): S_{yy} is positive at small light intensities due to the contribution of the linearly polarized beam, but at high light intensities the contribution from the circularly polarized beam provides the main effect and S_{yy} becomes negative.

At small light intensities, the Taylor series for the distribution function (9) can be used at small values of the parameter $V_0/kT \leq 1$, and we obtain the following asymptotic behavior of the component S_{yy} :

$$S_{yy} \cong \frac{V_0}{5kT} (1/3 - w_y) \text{ at } V_0/kT \leq 1. \quad (13)$$

It can be seen that the initial slope of the dependence $S_{yy}(V_0/kT)$ changes the sign at critical value $w_y = 1/3$: the slope is positive at $w_y < 1/3$ and negative at $w_y > 1/3$. Therefore, the order parameter S_{yy} demonstrates nonmonotonic behavior as a function of V_0/kT at $w_y < 1/3$ (as shown in Figure 2a), whereas S_{yy} is negative and decreases monotonically as a function of V_0/kT at $1/3 \leq w_y \leq 1/2$ (as presented in Figure 2b).

The components of the order parameter tensor as functions of the parameter w_y , which is related to the aspect ratio of the polarization ellipse, are shown in Figure 3 at different values of the parameter V_0/kT , which is proportional to the intensity of light. One can see

that at any values $0 < w_y < 1/2$ the biaxial ordering is observed with $S_{xx} \neq S_{yy} \neq S_{zz}$. At limiting cases $w_y = 0$ and $w_y = 1/2$ one can see uniaxial ordering: an ordered structure under linearly polarized light with $S_{xx} < 0$ ($S_{zz} = S_{yy}$) and an ordered structure under circularly polarized light with $S_{zz} > 0$ ($S_{xx} = S_{yy}$). As it was discussed above, $S_{xx} < 0$ and $S_{zz} > 0$ at any values of w_y , whereas the value S_{yy} changes the sign: it is positive at small values of w_y and it is negative at high values of w_y close to $1/2$. The value w_y , at which $S_{yy} = 0$, decreases with increasing intensity of light.

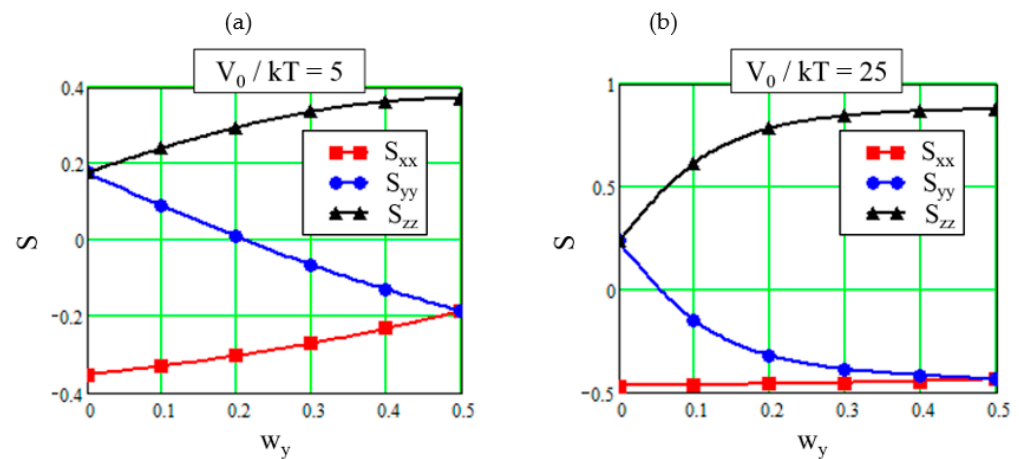


Figure 3. Components of the order parameter tensor $S_{\beta\beta}$ as functions of the parameter w_y at $V_0/kT = 5$ (a) and 25 (b).

The biaxial photo-ordering is accompanied by the light-induced deformation of azo-containing polymer networks.

4. Light-Induced Deformation of Azo-Containing Polymer Networks

The relationship between the biaxial orientation order and the deformation of Gaussian networks consisting of long polymer strands ($N \gg 1$) was analyzed in detail by us in ref. [34]. The extension ratios of an initially isotropic polymer network along the x, y, z -axes can be written in the following form [34]:

$$\lambda_x = \left(\frac{\langle l_x^2 \rangle^2}{\langle l_y^2 \rangle \langle l_z^2 \rangle} \right)^{1/6}, \quad \lambda_y = \left(\frac{\langle l_y^2 \rangle^2}{\langle l_x^2 \rangle \langle l_z^2 \rangle} \right)^{1/6} \quad \text{and} \quad \lambda_z = \left(\frac{\langle l_z^2 \rangle^2}{\langle l_x^2 \rangle \langle l_y^2 \rangle} \right)^{1/6}, \quad (14)$$

where $\langle l_\beta^2 \rangle$ ($\beta = x, y, z$) are the averaged projections of Kuhn segments on the x, y, z -axes. In turn, the orientation distribution of the Kuhn segments is related to the ordering of the azobenzene chromophores attached to them [34]:

$$\langle l_\beta^2 \rangle = \frac{l^2}{3} [1 + 2qS_{\beta\beta}]. \quad (15)$$

Here l is the length of the Kuhn segment, $S_{\beta\beta}$ are the components of the order parameter tensor for azo-chromophores considered in the previous section, and the structural parameter q is defined by the orientation distribution of azobenzenes around the Kuhn segments [34]:

$$q = \frac{3\langle \cos^2 \alpha \rangle_W - 1}{2}. \quad (16)$$

Here the averaging over the angle α is done with respect to the distribution function $W(\alpha)$. The structural parameter q changes in the range $[-1/2, 1]$. The value $q = -1/2$ describes azo-networks with orientation of the chromophores perpendicular to the back-

bones ($\alpha = 90^\circ$), whereas the value $q = 1$ corresponds to the main-chain polymers with the chromophores lying parallel to the backbones ($\alpha = 0^\circ$). Depending on the structure, the polymer network can demonstrate different photo-mechanical behavior.

Figure 4a,b shows the elongation ratios as functions of the parameter V_0/kT , which is proportional to the intensity of the light, for a polymer network with preferable orientation of azo-chromophores along the Kuhn segments ($q = 1$). The values of the parameter w_y are chosen in the ranges $0 < w_y < 1/3$ and $1/3 < w_y < 1/2$, as in Figure 2a,b. One can see that the biaxiality of the orientation ordering leads to the biaxial photo-deformation: $\lambda_x \neq \lambda_y \neq \lambda_z$. Alignment of the azo-chromophores and the Kuhn segments along the direction of light propagation ($S_{zz} > 0$) is accompanied by the expansion of the azo-network along this direction: $\lambda_z > 1$. The ordering of azo-chromophores aside the x -axis ($S_{xx} < 0$) leads to the contraction along the x -axes: $\lambda_x < 1$. Non-monotonical behavior of the order parameter S_{yy} as a function of light intensity at $0 < w_y < 1/3$ results in the similar behavior for elongation with respect to the y -axis.

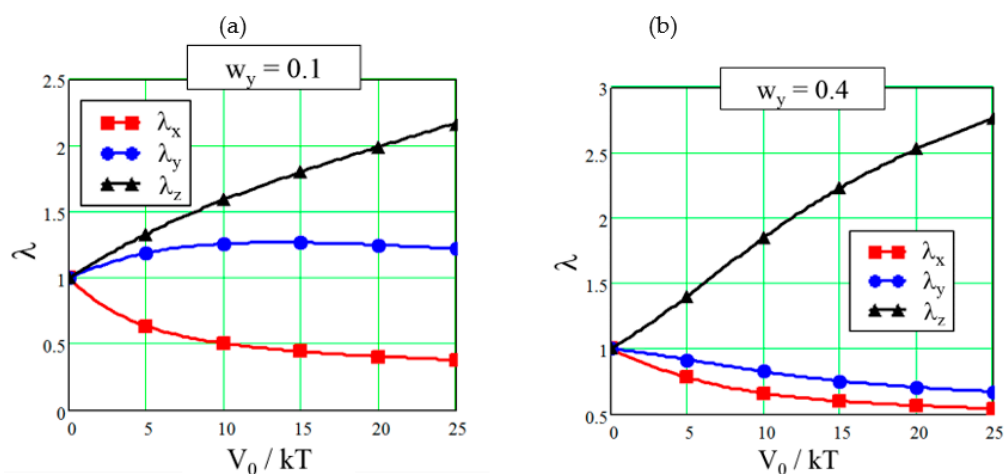


Figure 4. Elongation ratios $\lambda_{x,y,z}$ as functions of the parameter V_0/kT at $w_y = 0.1$ (a) and $w_y = 0.4$ (b) for an azo-network with $q = 1$.

An opposite photo-mechanical behavior is observed if the azo-chromophores are distributed perpendicularly to the Kuhn segments ($q = -1/2$), as it is shown in Figure 5. Figure 5a,b illustrates the dependences of elongation ratios $\lambda_{x,y,z}$ on the parameter V_0/kT at $w_y = 0.1$ (a) and $w_y = 0.4$ (b) for an azo-network with $q = -1/2$. It can be seen from Figure 5 that in this case the azo-network contracts with respect to the direction of light propagation ($\lambda_z < 1$) and expands with respect to the x -axis ($\lambda_x > 1$). Variation of the parameter q , which can be achieved by variation of the chemical structure and lengths of spacers, leads to the change of photo-mechanical response, as presented in Figure 6. At positive values of q , azo-networks demonstrate an expansion with respect to the direction of light propagation ($\lambda_z > 1$), whereas a contraction with respect to this direction is observed ($\lambda_z < 1$) at negative values of q . Thus, depending on the chemical structure, azo-polymers can demonstrate either expansion or contraction with respect to the direction of the propagation of light in agreement with experiments [2,36].

Finally, we discuss briefly the influence of the amount of azo-chromophores on the light-induced elastic deformation of azo-networks. In the considerations above, it was assumed that all Kuhn segments contain azo-chromophores in side chains. If some Kuhn segments do not contain azobenzene chromophores, they are not influenced by the light and are characterized by isotropic orientation distribution, for which the averaged value $\langle l_\beta^2 \rangle$ is given by $\langle l_\beta^2 \rangle = l^2/3$ ($\beta = x, y, z$). Taken into account the contributions from these segments, we can generalize Equation (15) and rewrite it in the following form:

$$\langle l_\beta^2 \rangle = \frac{l^2}{3} [1 + 2\phi q S_{\beta\beta}], \quad (17)$$

where ϕ is the number fraction of the Kuhn segments incorporating azobenzene side chains with respect to the total number of Kuhn segments in a network strand. According to Equation (17), the change of the number fraction ϕ is equivalent to the reduction of the parameter q . It can be seen from Figure 6 that the increase of the absolute value of the parameter q increases the magnitude of photo-deformation. Correspondingly, one can conclude that increase of the amount of azo-chromophores should amplify the photo-mechanical response of azo-polymers. The last result is in agreement with experimental data [1]. Thus, variation of the chemical structure of azobenzene-containing polymer networks allows to achieve target photo-mechanical properties necessary for practical applications.

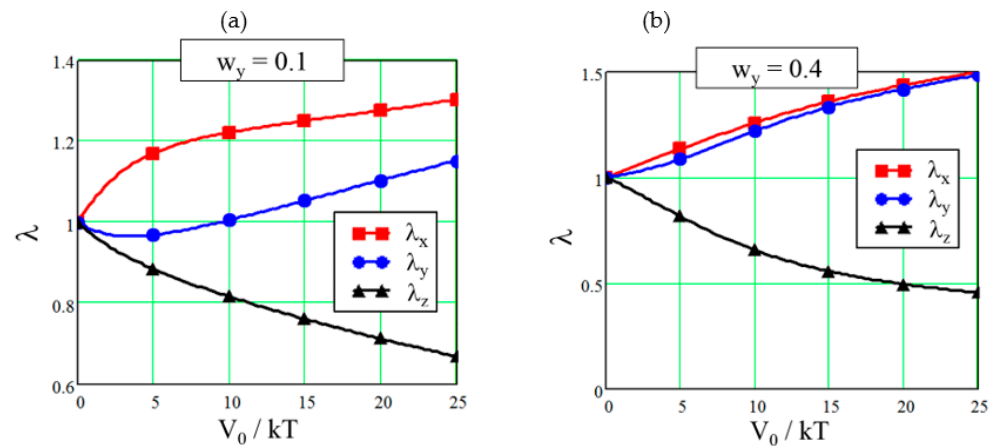


Figure 5. Elongation ratios $\lambda_{x,y,z}$ as functions of the parameter V_0/kT at $w_y = 0.1$ (a) and $w_y = 0.4$ (b) for an azo-network with $q = -1/2$.

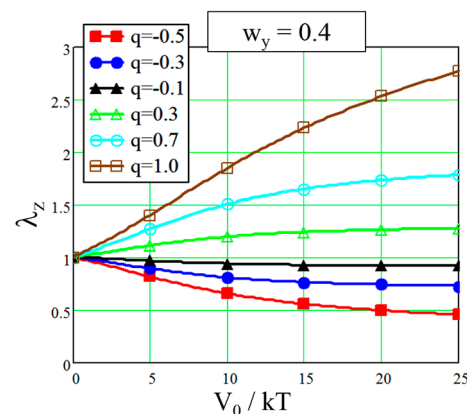


Figure 6. Elongation ratio λ_z as functions of the parameter V_0/kT at $w_y = 0.4$ and at varying structural parameter q .

5. Conclusions

The theory of light-induced ordering and deformation of azo-polymer networks under irradiation with elliptically polarized light is developed. An orientation potential, that aligns azobenzene chromophores perpendicular to the polarization of a light beam, has been proposed to describe photo-ordering in a steady state of cyclic trans-cis-trans angular-dependent photoisomerization. It has been shown that a biaxial photo-ordering and deformation appear under irradiation with elliptically polarized light. Azobenzene chromophores are oriented along the direction of light propagation and aside the direction of the maximal intensity of the light beam. The orientation order parameter with respect to the direction with minimal intensity of elliptically polarized light can be positive or negative, depending on the ratio between the maximal and minimal light intensity. Depending on the orientation distribution of azobenzenes around polymer backbones, the azo-network

either expands or contracts with respect to three principal axes related to the light beam of elliptical polarization. The results of the theory are useful for practical application to create azobenzene polymers with demanded photo-mechanical response under irradiation with light of specific polarization, depending on their chemical structure.

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